

## Feasibility of measuring dissolved carbon dioxide based on head space partial pressures

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### Abstract

We describe an instrument prototype that measures dissolved carbon dioxide (DC) without need for standard wetted probe membranes or titration. DC is calculated using Henry's Law, water temperature, and the steady-state partial pressure of carbon dioxide that develops within the instrument's vertical gas–liquid contacting chamber. Gas-phase partial pressures were determined with either an infrared detector (ID) or by measuring voltage developed by a pH electrode immersed in an isolated sodium carbonate solution (SC) sparged with recirculated head space gas. Calculated DC concentrations were compared with those obtained by titration over a range of DC (2, 4, 8, 12, 16, 20, 24, and 28 mg/l), total alkalinity (35, 120, and 250 mg/l as CaCO<sub>3</sub>), total dissolved gas pressure (–178 to 120 mmHg), and dissolved oxygen concentrations (7, 14, and 18 mg/l). Statistically significant ( $P < 0.001$ ) correlations were established between head space (ID) and titrimetrically determined DC concentrations ( $R^2 = 0.987$ – $0.999$ ,  $N = 96$ ). Millivolt and titrimetric values from the SC solution tests were also correlated ( $P < 0.001$ ,  $R^2 = 0.997$ ,  $N = 16$ ). The absolute and relative error associated with the use of the ID and SC solution averaged 0.9 mg/l DC and 7.0% and 0.6 mg/l DC and 9.6%, respectively. The precision of DC estimates established in a second test series was good; coefficients of variation ( $100(\text{SD}/\text{mean})$ ) for the head space (ID) and titration analyses were 0.99% and 1.7%. Precision of the SC solution method was 1.3%. In a third test series, a single ID was coupled with four replicate head space units so as to permit sequential monitoring (15 min intervals) of a common water source. Here, appropriate gas samples were secured using a series of solenoid valves (1.6 mm bore) activated by a time-based controller. This system configuration reduced the capital cost per sample site from US\$

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2695 to 876. Absolute error averaged 2.9, 3.1, 3.7, and 2.7 mg/l for replicates 1–4 ( $N = 36$ ) during a 21-day test period (DC range, 36–40 mg/l). The ID meter was then modified so as to provide for DO as well as DC measurements across components of an intensive fish production system.

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## 1. Introduction

Water requirements for intensive fish culture have been reduced through integration of water recirculation and water treatment processes, including gas transfer. Here, control of dissolved carbon dioxide (DC) is important given its ability to cause nephrocalcinosis (Smart et al., 1979) and to reduce the ability of blood to transport oxygen (Basu, 1959). High concentrations of DC can also reduce pH below acceptable limits in waters of low alkalinity (Colt and Orwicz, 1991). Given that carbon dioxide excretion rates vary with time, control costs are reduced when equipment is designed to match gas transfer rates with gas transfer needs. Feedback control loops can satisfy this requirement (Watten et al., 1994), but rely on robust dissolved gas sensors. Unfortunately, standard methods for measurement of DC (APHA, 1998) are limited to either titration or use of a nomograph requiring bicarbonate alkalinity, temperature, pH and total dissolved solids. We consider both methods unsuitable for continuous monitoring given labor requirements and changes in alkalinity with time related to nitrification (Haug and McCarty, 1972). Further, titration errors increase with the concentration of certain dissolved compounds common in aquaculture including ammonia, nitrite, phosphate and seawater salts (APHA, 1998). DC probes provide an alternative method of measurement but gas-permeable membranes separating probe electrolyte (sodium bicarbonate) and a pH-sensing element from water are susceptible to biological fouling (Speirs et al., 1986; Watten et al., 1997). Dissolved gases have also been monitored using chromatographic methods (Swinnerton et al., 1962; Williams and Miller, 1962). Here, dissolved gasses are stripped from solution by sparging with an inert carrier gas, such as helium, or by directing the carrier gas through an isolated mechanical device that provides needed gas–liquid interfacial area. The resulting gas mixture is then identified with a gas chromatograph. This method is sensitive to variations in gas and liquid flow rate and is expensive. Watten (1992) described a dissolved oxygen (DO) monitoring system that circumvents the high cost of chromatography and problems associated with wetted gas-permeable membranes. DO is calculated using Henry's Law, water temperature, and the partial pressure of oxygen that develops in the head space of a vertical gas–liquid contacting chamber. Water enters the chamber as a spray, then exits into a receiving basin through a cone diffuser designed to minimize bubble carryover. Head space gas composition, measured with a galvanic oxygen sensor, changes as an equilibrium is established between gas-phase partial pressures and dissolved gas tensions. Calculated DO concentrations were compared with those obtained by Winkler analysis over a range of DO, water temperature, and dissolved nitrogen levels. Differences between the two analytical methods averaged just 0.25 mg/l (range –0.51 to 0.86 mg/l). Time required to reach 90% of equilibrium DO concentrations averaged 8.6 min which was sufficient to adequately follow changes in DO of about 26 mg/l h.

In this study we modified the instrument described by Watten (1992) so as to provide estimates of DC through measurement of CO<sub>2</sub> in head space gas, either with an infrared detector (ID) or through measurement of [H<sup>+</sup>] in a carbonate solution sparged with head space gas. Instrument accuracy and precision was then assessed over a range of DC–DO temperature, alkalinity, and total dissolved gas concentrations. Further, we tested the performance of a single ID coupled to four replicate gas–liquid contacting chambers operated in parallel.

## 2. Instrument description

The test instrument was designed to promote equilibrium between dissolved gas tensions ( $P_i^L$ ) and gas phase partial pressures ( $P_i^G$ ) within a gas–liquid contacting chamber (Fig. 1). Thus, for individual gas species:

$$P_i^L = P_i^G \quad (1)$$

and for all gases present:

$$\left( \sum_i^n P_i^L \right) + P_{H_2O} = \left( \sum_i^n P_i^G \right) + P_{H_2O} \quad (2)$$

where  $P_{H_2O}$  represents water vapor pressure (Colt, 1984), and all  $P$  values are expressed in mmHg. From Dalton's Law, the sum of terms on the right side of Eq. (2) represents total gas phase pressure (absolute). The sum on the left side represents total dissolved gas pressure (TGP). The head space chamber is vented to the atmosphere to prevent internal water level fluctuations that may result from gas absorption or release by water directed through the instrument. Hence, the equalities given in Eq. (1) and (2) will be true only when the TGP is equal to atmospheric pressure (BP), i.e.  $\Delta P$  is 0 where

$$\Delta P = TGP - BP \quad (3)$$

and BP is atmospheric pressure in mmHg.

Hypobaric ( $\Delta P < 0$ ) and hyperbaric  $\Delta P > 0$  conditions will cause gas movement into and out of the head space chamber, respectively. This action will result in some deviation of  $P_i^G$  from  $P_i^L$ . The instrument design shown (Fig. 1) provides for the measurement of head space partial pressure ( $P_{CO_2}^G$ ) using an infrared sensor that incorporates an internal gas-sampling pump (Model PM300 Infrared Gas Analyzer, C.E.A. Instruments, Emerson, NJ, USA). This instrument provides a percent by volume CO<sub>2</sub> measurement from which  $P_{CO_2}^G$  is calculated:

$$P_{CO_2}^G = BP \left( \frac{\%CO_2}{100} \right) \quad (4)$$

$P_{CO_2}^G$  values estimate carbon dioxide tension ( $P_{CO_2}^L$ , Eq. (1)), from which DC can be established (mg/l) given water temperature, salinity, and appropriate Bunsen solubility

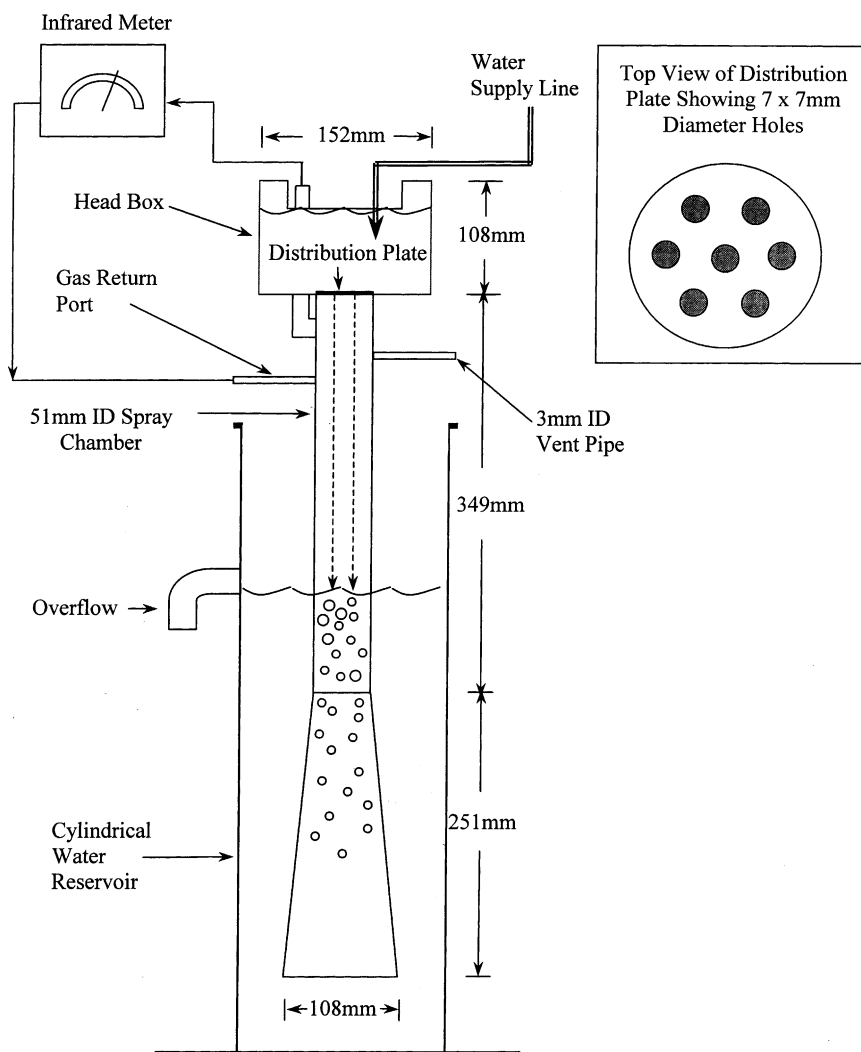


Fig. 1. Dimensions of the head space instrument shown coupled with an infrared meter that measures gas-phase concentrations of carbon dioxide.

coefficients ( $\beta$ ), i.e. from Henry's Law (Colt, 1984):

$$DC = \beta_{\text{CO}_2} \left( \frac{P_{\text{CO}_2}^L}{0.3845} \right) \quad (5)$$

where  $\beta_{\text{CO}_2}$  is in units of l gas/l water-atmosphere, and  $P_{\text{CO}_2}^L$  is in units of mmHg. The factor 0.3845 equals  $760/(1000 k)$  and  $k$  represents the ratio of molecular weight to molecular volume for carbon dioxide gas (Colt, 1984). Our alternate instrument design provides for the indirect measurement of  $P_{\text{CO}_2}^G$  by recirculating head space gas through a sparger submerged

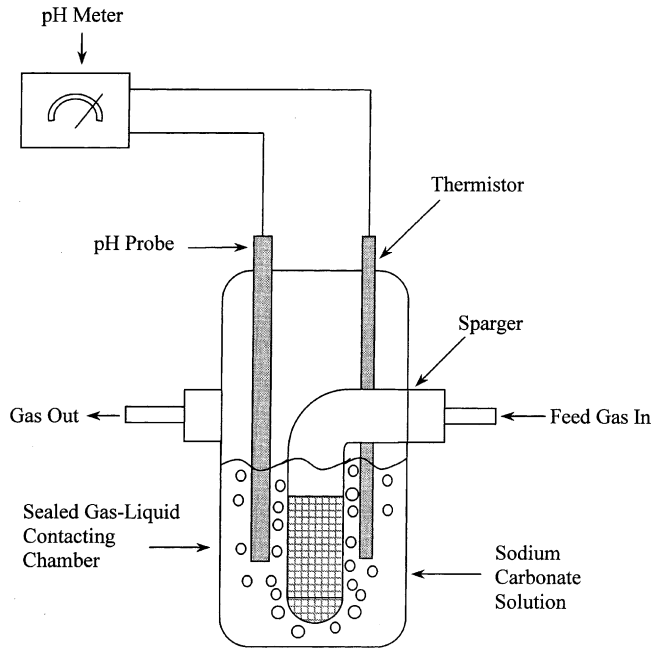
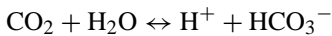


Fig. 2. Section view of the closed sparging system used to measure gas-phase concentrations of carbon dioxide based on changes in carbonate solution pH.

in an isolated sodium carbonate (SC) solution (Fig. 2). The sparger promotes movement of  $\text{CO}_2$  into or out of the SC solution so that the following equilibrium can be established:

$$P_{\text{CO}_2}^{\text{L}} = P_{\text{CO}_2}^{\text{G}} = P_{\text{CO}_2}^{\text{SC}} \quad (6)$$

Induced changes in  $P_{\text{CO}_2}^{\text{SC}}$  affect the hydrogen ion concentration in the SC solution:



The relationship between DC, water, bicarbonate and hydrogen ion is obtained from the Law of Mass Action:

$$\frac{[\text{H}^+]^{\text{SC}} [\text{HCO}_3^-]^{\text{SC}}}{[\text{DC}]^{\text{SC}}} = \text{constant} \quad (7)$$

Since the SC solution contains a high concentration of sodium bicarbonate, the  $[\text{HCO}_3^-]^{\text{SC}}$  term can be treated as a constant. Hence:

$$[\text{H}^+]^{\text{SC}} = [\text{DC}]^{\text{SC}} \text{constant} \quad (8)$$

We measure  $[\text{H}^+]^{\text{SC}}$  electrometrically using a temperature-compensated pH probe sealed in the sparging vessel. The electrical potential of the pH probe (mV) is related to  $[\text{H}^+]^{\text{SC}}$  by the Nernst equation:

$$E = E_0 + S \times \log[\text{H}^+]^{\text{SC}} \quad (9)$$

where  $E$  is the measured potential (mV),  $E_0$  the reference potential (a constant), and  $S$  is the electrode slope. Given that  $[H^+]$  is directly related to DC (Eq. (8)) electrode response to DC follows Eq. (9):

$$E = E_0 + S \times \log[DC]^{SC} \quad (10)$$

Solving Eq. (10) for  $[DC]^{SC}$  allows indirect measurement of  $[DC]^L$  based on Eq. (5) and (6). Gas void space, water flow rate, spray fall, SC volume, and SC sparging rate affect the response of  $E$  to changes in DC. Our instrument (Fig. 1) incorporated six 1 cm jet ports that allow a water throughput of about 12 l/min, and a spray zone of about 26 cm. The SC solution volume was fixed at 340 ml, and was contained in a modified 1 l sample bottle (Fig. 2).

### 3. Methods

#### 3.1. Test series I

We compared test instrument-derived DC concentrations with those established by standard titration (APHA, 1998). DC was first measured with influent DC concentrations of about 2, 4, 8, 12, 16, 20, 24 and 28 mg/l under each of six different water quality regimes. The regimes included a low, medium, and high DO (about 7, 14, and 18 mg/l); low, medium, and high total alkalinity (ALK) (about 35, 120, 250 mg/l as  $CaCO_3$ ); and low and high  $\Delta P$  (−178 to 115 mmHg). The procedure resulted in a total of 48 different operating conditions, each of which was replicated once. All tests were conducted using well water (about 10 °C).

Test water was first pumped through a portable vacuum degasser (Watten et al., 1994) and then into a 200 l head tank. Water was pumped from the tank through a variable area flowmeter, and then into the head box of the test instrument. The influent DO and DC were altered, when necessary, by metering oxygen and carbon dioxide into the packed column component of the vacuum degasser. Total alkalinity was enhanced by metering a concentrated solution of sodium bicarbonate into the same degassing system via a peristaltic pump. Likewise, DO was lowered by metering a solution of sodium sulfite with cobalt added as a catalyst (16 g of sodium sulfite and 0.16 g cobalt chloride per liter) and DC was removed by metering a concentrated solution of sodium hydroxide. During these tests, the  $CO_2$  level in the instrument's head space was measured with the ID and used to calculate DC ( $DC_{hs}$ ) based on Eqs. (4) and (5), water temperature, and Bunsen solubility coefficients from Colt (1984). A water sample was also taken from the instrument's head box for DC measurement ( $DC_t$ ) by titration (APHA, 1998). Other variables measured included DO (Model 57 DO Meter, Yellow Springs Instrument, Yellow Springs, OH, USA), total alkalinity (APHA, 1998), pH (Solomat Modumeter 2019, Model 2007 pH module electrode, Solomat, Stamford CT, USA), BP (Solomat Modumeter 2019), temperature (Hg thermometer) and  $\Delta P$  (Bouck, 1982). All readings were taken following stabilization of head space  $CO_2$  readings. Least squares regression analysis was used to correlate  $DC_t$  with  $DC_{hs}$  and the test variables ALK, DO,  $\Delta P$ , and BP. Further, head space and all other readings were repeated 10 times to establish  $DC_{hs}$  for a single DC concentration (9.8 mg/l) using oxygenated well water (10 °C).  $DC_{hs}$  was then compared to  $DC_t$  concentrations to establish an estimate of precision (coefficient of variation,  $100 S.D./\bar{x}$ ), as well as accuracy (relative and absolute error).

### 3.2. Test series II

We evaluated the feasibility of using the SC solution  $[H^+]$  to measure  $DC_{hs}$ . Initially, a mixture of air and carbon dioxide was directed through the sparging system (Fig. 2) outfitted with a pH and temperature probe (Solomat Modumeter 2019 with Model 2007 pH module electrode, Solomat, Stamford, CT, USA). We measured the response of probe pH and mV potential at two different concentrations of sodium carbonate (0.002 and 0.004N) to gas mixtures representing 0.1–1.3%  $CO_2$  on a volumetric basis as determined by the Model PM300 Infrared Gas Analyzer. Further, to establish precision, we repeated measurements of electrode potential ( $N = 9$ ) with the gas composition fixed at 0.8 %  $CO_2$  using the 0.004 N solution. The SC solution temperatures were fixed at 20 °C. Regression analysis was used to model measured electrode potentials (mV) versus gas composition (%  $CO_2$ ). We then coupled the sparging system to the head space instrument, in lieu of the ID, using a peristaltic pump to create a gas recirculation loop. With oxygenated well water (about 10 °C) flowing through the test instrument, we measured SC solution (0.004 M) pH and mV potential at  $DC_t$  concentrations of about 3, 5, 8, 12, 17, 19, 23 and 28 mg/l. DC was altered and all other test variables were measured as described in test series I.  $DC_{hs}$  was calculated for comparison with paired  $DC_t$  using the regression of electrode potential versus %  $CO_2$  (0.004N SC solution) and Eqs. (4) and (5).

### 3.3. Test series III

We evaluated accuracy and precision of  $DC_{hs}$  provided by a single ID coupled with four replicate head space instruments (Fig. 3). This system allowed monitoring of a common spring water source at intervals of 15 min over a 21-day period. Here, gas samples were drawn sequentially from replicate instruments through use of three-way solenoid valves (9VDC-1.6 mm Model P-01367-72, Cole Palmer Corporation, Vernon Hills, IL, USA), a programmable four-circuit valve controller (Model XT, Chrontrol Corporation, San Diego, CA, USA) and a CEA type ID (Model GD 444, CEA Instruments, Emerson, NJ, USA). The ID included a second timer programmed to synchronize activation of the internal gas sampling pump and data logger with valve sequencing. The ID was modified so that the gas exiting the infrared sensor was shunted outside the instrument's case via a 34 cm length of 3 mm diameter tubing. This modification prevented dilution of the head space gas samples with air at the end of the selected 30 s-pumping interval. Gas samples were not returned to their respective head space instruments so as to reduce system complexity. Therefore, gas return ports (Fig. 1) were plugged. On the suction side of the gas sample pump, we used 127 cm lengths of 1.6 mm diameter tubing (Model 95702-01, Cole Palmer, Vernon Hills, IL, USA) to couple components serving each replicate instrument. Logged data was recovered daily as were results of ID calibration checks against certified gas standards. Water samples were taken daily for DC measurement by titration (APHA, 1998) at about 9 AM and 3 PM except on day 7, 14 and 21 (9 AM only). Concurrently, we measured DO (Model 58, Yellow Springs Instrument, Yellow Springs, OH, USA), temperature,  $\Delta P$ , and BP (Model DS1-A Satrometer, Sweeny Aquametrics, Stony Creek, CT, USA).  $DC_{hs}$  was then calculated based on Eqs. (4) and (5) for comparison. On days 15–21, we removed gas tubing from the sample ports on replicate instruments one and three so that the ambient air, and not the

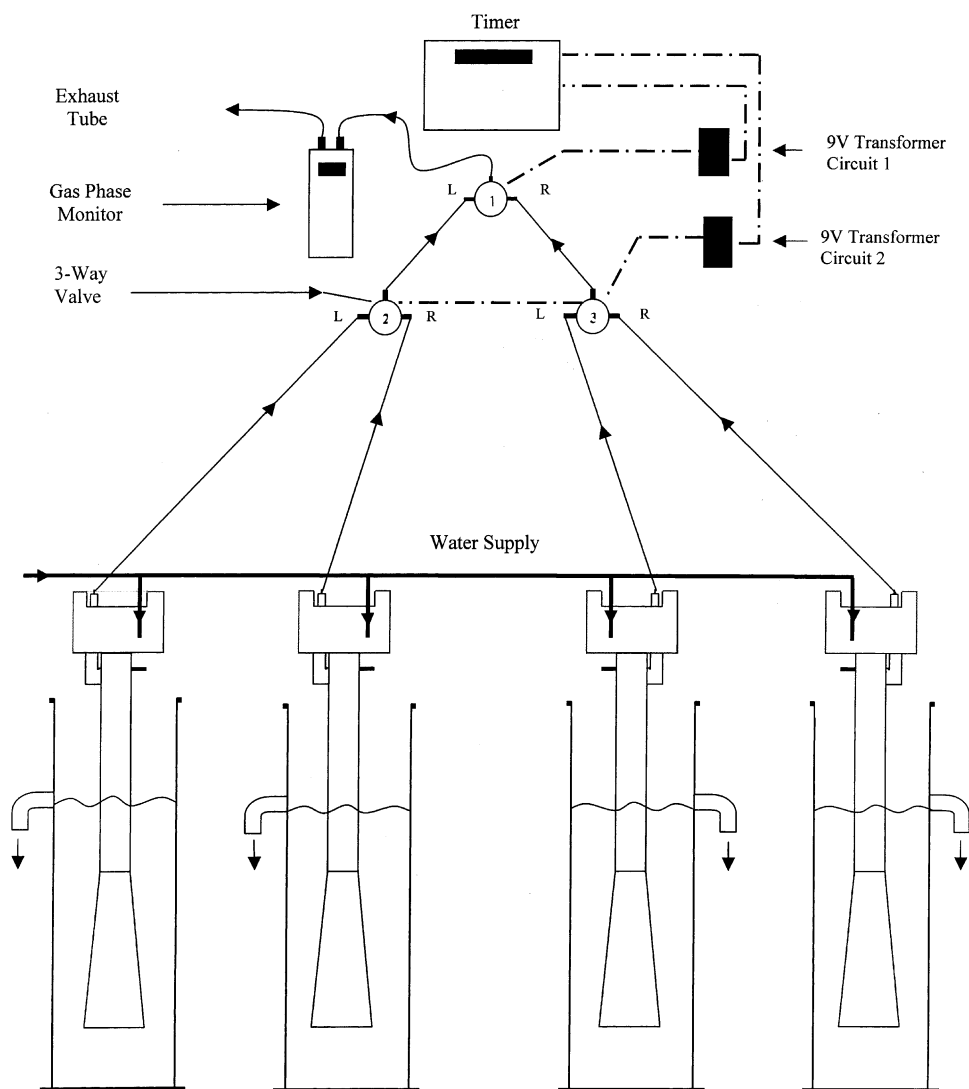


Fig. 3. Schematic of flows in the test system that coupled a single ID with four replicate head space instruments. The ID had its own time based gas sampling pump and data logger.

head space gas, was sampled. Here we tested the accuracy of  $DC_{hs}$  estimates provided by replicates two and four over an increased range of preceding sample  $P_{CO_2}^G$  values. Further, we coupled the head space instrument system (Fig. 3) to certain components of a recirculating water, fish production system—a  $CO_2$  stripper and a biological filter. The ID used (Model GD444  $PCO_2$  Plus, CEA Instruments, Emerson, NJ, USA) provided measurement of both % $CO_2$  and % $O_2$  for calculation of  $DC_{hs}$  and  $DO_{hs}$  changes across each component (inlet–outlet). Using methods just described, we measured temperature, BP, and DO once



or twice daily over a four-day test period.  $DC_t$  was measured using a HACH model digital titrator coupled with a 0.364 N NaOH reagent cartridge (HACH, Loveland, CO, USA).

Statistical analyses supporting test series I–III were completed using either the Statistical Analysis System (SAS, version 8.0) or Sigma Stat (version 2.0) software. Specific analyses included Student's  $t$  analysis of variance, linear regression, multiple linear regression and the Mann–Whitney's rank sum test.

## 4. Results

### 4.1. Test series I

Table 1 gives the DC,  $\Delta P$ , DO, ALK and temperature means established for test conditions 1–6. BP ranged between 727 and 736 mmHg. Good agreement existed between  $DC_t$  and  $DC_{hs}$  (Fig. 4). Results of the corresponding regression analyses are summarized in Table 2. Individual regressions were linear ( $R^2 > 0.98$ ) and statistically significant ( $P < 0.001$ ). Regression derived intercept coefficients and line slopes averaged 0.66 mg/l and 0.94, respectively. Multiple regression analysis performed with all the six treatments pooled found a significant correlation ( $R^2 = 0.99$ ;  $P < 0.001$ ) between test conditions,  $DC_{hs}$ , certain interaction terms and  $DC_t$ :

$$\begin{aligned} DC_t = & -69.2066 + 6.8139(DC_{hs}) + 0.0143(\Delta P) - 0.0142(DO) \\ & - 0.0008(ALK) + 0.0951(BP) - 0.0006(DC_{hs} * ALK) \\ & - 0.0080(DC_{hs} * BP) - 0.0020(\Delta P * DO) \end{aligned} \quad (11)$$

The mean of absolute and relative errors between estimates of  $DC_t$  (standard treatment) and  $DC_{hs}$  (comparison treatment) are summarized in Table 2. The lowest errors

Table 1  
Summary of conditions used to evaluate the accuracy of the test instrument when coupled to an infrared gas-phase sensor<sup>a</sup>

Variable		Test condition					
		1	2	3	4	5	6
DC (mg/l)	$\bar{x}$	14.3	14.2	14.4	14.5	14.2	14.7
	S.D.	9.1	9.2	9.0	9.2	9.1	8.6
DO (mg/l)	$\bar{x}$	13.3	17.8	7.4	13.1	8.0	13.9
	S.D.	0.1	0.5	0.4	0.1	0.0	0.1
Alkalinity (mg/l)	$\bar{x}$	35.1	34.7	35.7	118.7	36.8	247.7
	S.D.	3.7	3.3	2.5	13.1	4.4	6.7
$\Delta P$ (mmHg)	$\bar{x}$	-77	-21	-178	-72	115	-71
	S.D.	1.8	7.5	6.8	4.2	3.1	5.7
Temperature (°C)	$\bar{x}$	11.6	10.7	10.4	10.1	10.0	10.2
	S.D.	0.5	0.2	0.2	0.2	0.1	0.3

<sup>a</sup>  $N = 16$  in each condition tested (total  $N = 96$ ).

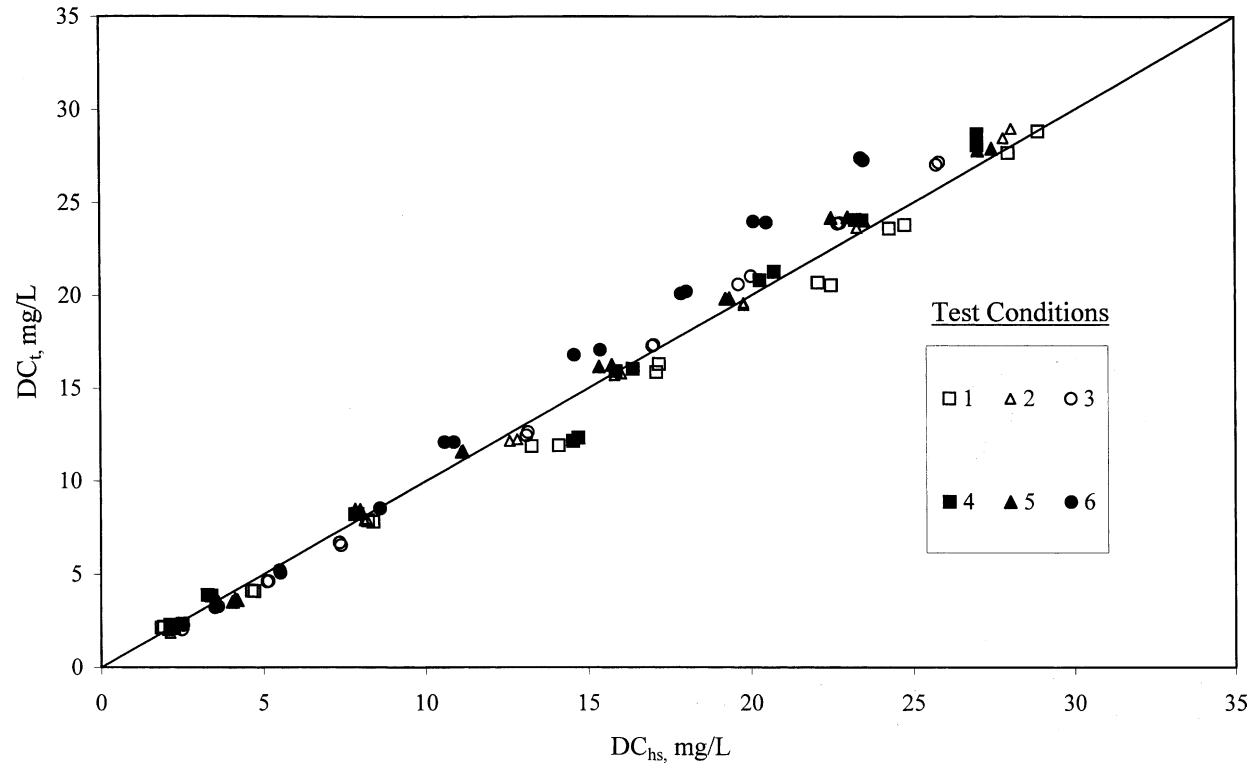


Fig. 4. Comparison of dissolved carbon dioxide estimates based on head space analyses ( $DC_{hs}$ ) with estimates based on titration ( $DC_{hs}$ ) under each of the six test conditions established in the test series I.

Table 2

Summary of regression analyses and errors established for operating conditions used in test series I

Variable		Test condition					
		1	2	3	4	5	6
Error (mg/l) <sup>a</sup>	$\bar{x}$	0.84	0.34	0.75	0.78	0.63	1.85
	Range	0.04–2.18	0.03–0.94	0.26–1.38	0.17–2.39	0.08–1.70	0.28–3.89
Relative error (%) <sup>b</sup>	$\bar{x}$	8.3	3.3	7.0	7.0	5.6	14.9
	Range	0.1–15.8	0.9–9.7	1.9–17.7	0.4–17.4	1.7–13.8	5.1–24.0
Linear regression <sup>c</sup>	Intercept	0.500	0.494	1.008	0.495	0.228	1.235
	Slope	1.019	0.967	0.915	0.957	0.951	0.810
	$R^2$	0.995	0.999	0.998	0.987	0.998	0.998
	$P$	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

<sup>a</sup> Error = abs (titration – gas phase values).<sup>b</sup> Relative error = Error/titration value.<sup>c</sup>  $Y = a + bX$ , where  $Y$  = DC titration value, mg/l;  $a$  = intercept, mg/l;  $b$  = slope, dimensionless;  $X$  = DC gas phase value, mg/l.

were obtained during the high DO and low ALK treatment, while the highest relative and absolute errors occurred in the high ALK and medium DO treatment. The absolute error associated with the use of the head space instrument overall averaged 0.9 mg/l ( $N = 96$ ). The corresponding mean relative error was 7.0%. Differences between  $DC_t$  and  $DC_{hs}$  ranged from  $-4.0$  to  $2.4$  mg/l, with a mean of  $-0.3$  mg/l and a skewness statistic of  $-0.88$ . During subsequent precision tests, operating conditions were  $\Delta P$ ,  $-73$  mmHg (S.D. = 1.62); DO, 14.2 mg/l (S.D. = 0.04); ALK, 32.6 mg/l (S.D. = 0.39); and BP, 733 mmHg (S.D. = 0.42). Here  $DC_{hs}$  exceeded  $DC_t$  ( $P < 0.001$ ) with a mean difference of 0.3 mg/l (S.D. = 0.11), i.e. a mean of 9.8 mg/l (S.D. = 0.10) versus 9.5 mg/l (S.D. = 0.16). The coefficient of variation for  $DC_{hs}$  and  $DC_t$  was 0.97 and 1.70%, respectively. Differences between DC means were not significant ( $P > 0.05$ ).

#### 4.2. Test series II

The time required to establish equilibrium conditions within the sparger assembly was about 9 min. Fig. 5 gives the correlation between electrode potential (mV) and gas composition (%) for both the SC solutions tested. The range of mV values shown corresponds to pH ranges of 6.97–8.07 (0.002N) and 7.17–8.37 (0.004N). Both correlations were statistically significant as determined by regression analysis following data transformation ( $\log \%CO_2$ ):

##### 1. 0.002 N SC solution

$$\text{Electrode potential (mV)} = -14.993 + (55.791 \times \log(\%CO_2)) \quad (12)$$

$$R^2 = 0.999; P < 0.001; \text{S.E.} = 0.753 \text{ mg/l}$$

##### 2. 0.004 N SC solution

$$\text{Electrode potential (mV)} = -33.593 + (58.472 \times \log(\%CO_2)) \quad (13)$$

$$R^2 = 0.998; P < 0.001; \text{S.E.} = 1.14 \text{ mg/l}$$

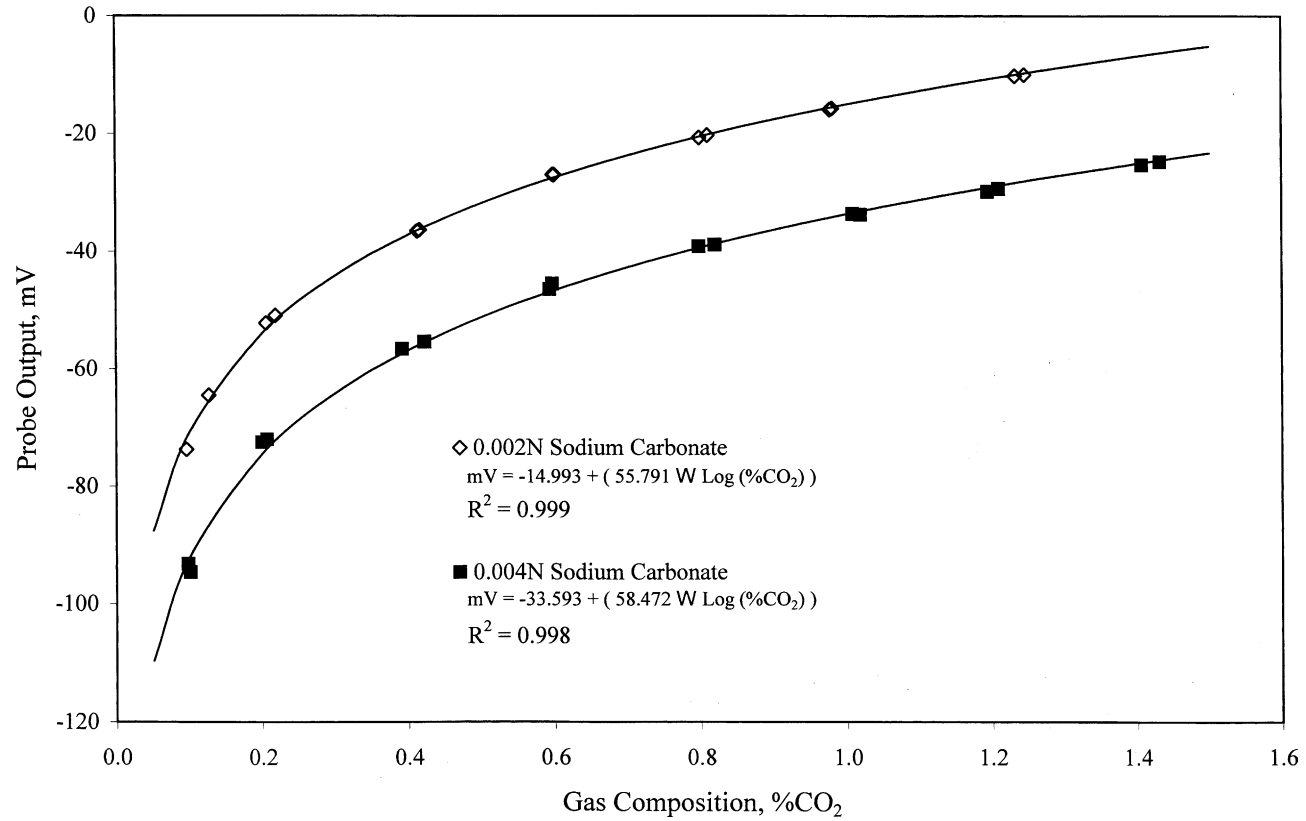


Fig. 5. Response of electrode output (mV) to changes in composition of gas (%CO<sub>2</sub>) directed through the test sparging system shown in Fig. 2.

These models are in agreement with the theoretical response of electrode potentials predicted by Eq. (10). Replicate measurements of probe potentials with CO<sub>2</sub> fixed at 0.8% averaged  $-39.37$  mV with a coefficient of variation of 1.0%. With the sparging system coupled to the head space instrument, test conditions were:  $\Delta P$ , 71 mmHg (S.D. = 2.88); DO, 13.8 mg/l (S.D. = 0.07); ALK, 34.0 mg/l (S.D. = 4.78); BP, 733 mmHg (S.D. = 1.26). Good agreement exists between resultant DC<sub>t</sub> and DC<sub>hs</sub> values (Fig. 6). Regression analysis indicates the correlation is linear and statistically significant:

$$DC_t \text{ (mg/l)} = 1.156 + (0.944 \times DC_{hs}) \quad (14)$$

$$R^2 = 0.999; P < 0.001; \text{S.E.} = 0.32$$

The means of absolute and relative errors associated with DC<sub>hs</sub> (DC<sub>t</sub> – DC<sub>hs</sub>) were 0.6 mg/l (S.D. = 0.41) and 9.6% (S.D. = 12.3). Errors ranged from  $-0.5$  to 1.3 mg/l with a mean of 0.4 mg/l (S.D. = 0.60). Here the skewness statistic was 0.86. Differences between mean values of DC<sub>t</sub> and DC<sub>hs</sub> for the group were not statistically significant ( $P < 0.05$ ). Fig. 7 shows changes in electrode potential with DC<sub>t</sub> are again in agreement with Eq. (10). The regression equation describing the relationship is:

$$\text{Electrode potential (mV)} = -127.116 + (69.486 \times \log(DC_t)) \quad (15)$$

$$R^2 = 0.997; P < 0.001; \text{S.E.} = 1.379$$

Electrode potentials established during precision tests were converted to DC<sub>t</sub> with Eq. (15) so as to express results in units of mg/l. Predicted DC<sub>t</sub> averaged 18.3 mg/l with a range of 18.0–18.7 mg/l. The coefficient of variation was 1.32%.

### 4.3. Test series III

Integration of the single ID with 4 replicate head space instruments reduced capital costs per station from US\$ 2695 to 876. During the initial 21-day trial, electronic drift of the ID was minor ( $< 0.09\%$  CO<sub>2</sub>) and recalibration of the instrument was not required. Here, DO,  $\Delta P$ , temperature, and BP averaged 10.6 mg/l (S.D. + 0.95), 25 mmHg (S.D. = 3.3), 14.1°C, and 747 mmHg (S.D. = 2.4), respectively. DC<sub>t</sub> averaged 38.2 mg/l (S.D. = 1.0,  $N = 36$ ) and did not vary significantly ( $P > 0.05$ ) with time. Corresponding values for DC<sub>hs</sub> (all replicates) averaged 35.3 mg/l (S.D. = 2.1), resulting in a mean calculated error (DC<sub>t</sub> – DC<sub>hs</sub>) of  $-2.9$  mg/l (S.D. = 2.4). This equates to a relative error of 8.2%, with a coefficient of variation of 6.8%. Absolute error averaged 2.9, 3.1, 3.7, and 2.7 mg/l for replicates 1–4. Differences between DC<sub>t</sub> and DC<sub>hs</sub> groups were statistically significant ( $P < 0.05$ ). Precision, as measured by the SD of replicate DC<sub>hs</sub> estimates (1–4), averaged 0.46 (S.D. = 1.5) with a corresponding coefficient of variation ((S.D.  $\times$  100)/mean DC<sub>hs</sub>) of 1.3%. Precision and error of DC<sub>hs</sub> estimates did not vary significantly with time ( $P > 0.5$ ) despite measurement of ambient air (replicates 1 and 3) during 15–21 days. During the second trial of 4 days, water temperature averaged 12.9 °C while BP ranged between 732–750 mmHg. Fig. 8 gives example DO<sub>hs</sub> and DC<sub>hs</sub> values for the inlet and outlet of a treatment unit. In all stations monitored, DO<sub>hs</sub> ranged between 5.9–10.5 mg/l. Error of DO<sub>hs</sub> estimates (DO<sub>hs</sub> – DO<sub>probe</sub>), overall, averaged 1.1 mg/l (S.D. = 0.8,  $N = 28$ ) with a range of 0.0–2.5 mg/l. The corresponding relative error was 12.9%. Associated DC<sub>hs</sub> values ranged between 14.5 and 29.7 mg/l with a mean of 22.2 mg/l. Here error (DC<sub>t</sub> – DC<sub>hs</sub>) averaged

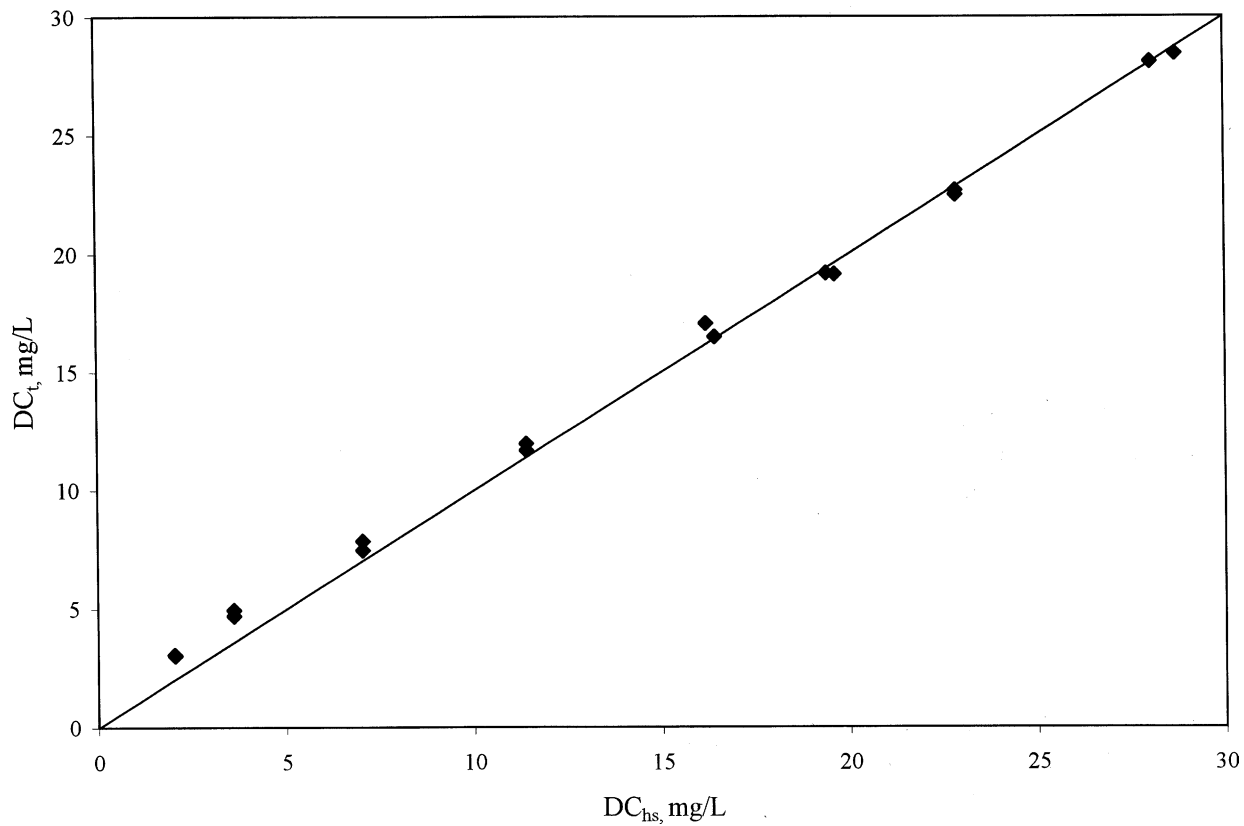


Fig. 6. Comparison of dissolved carbon dioxide estimates based on head space analyses ( $DC_{hs}$ ) with estimates based on titration ( $DC_t$ ) measured during the test series II.

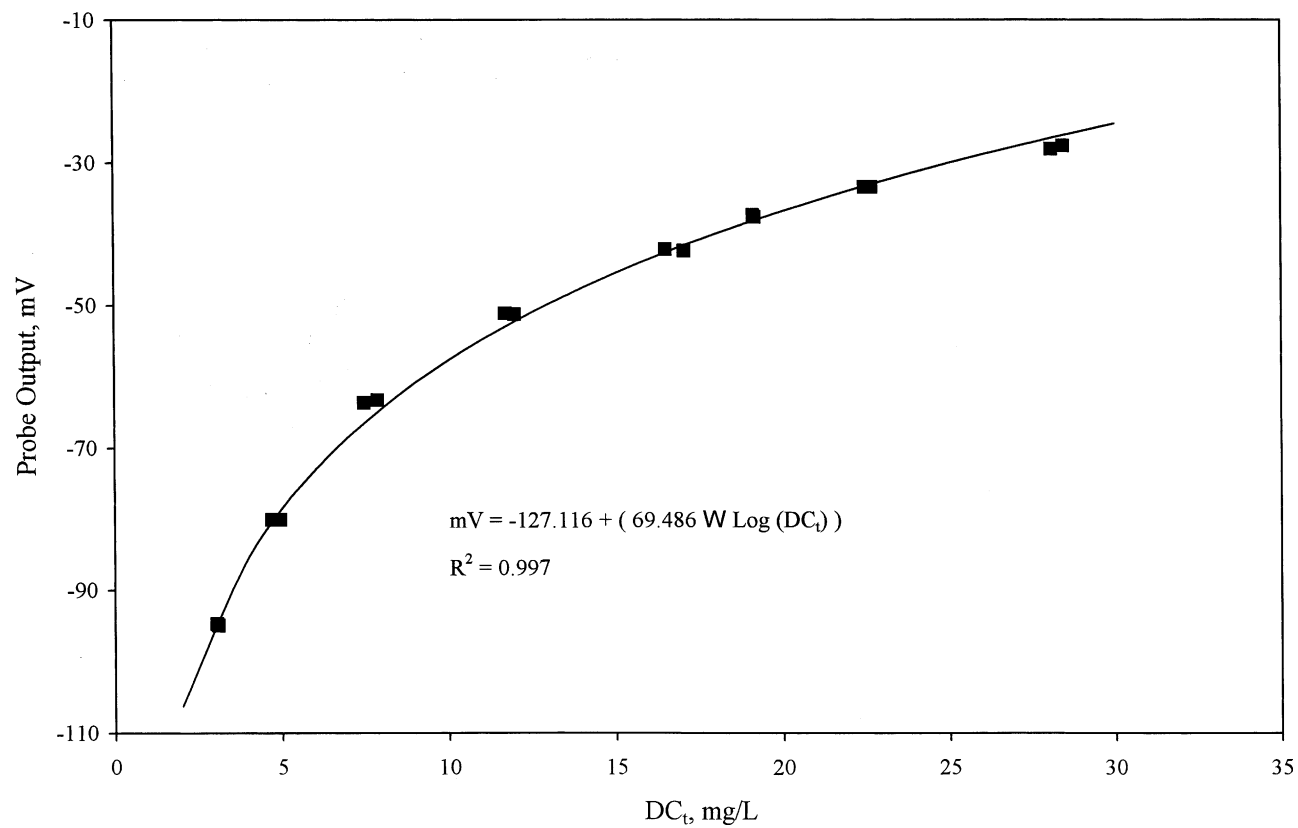


Fig. 7. Response of electrode output (mV) to changes in dissolved carbon dioxide (DC<sub>t</sub>) observed in test series II.

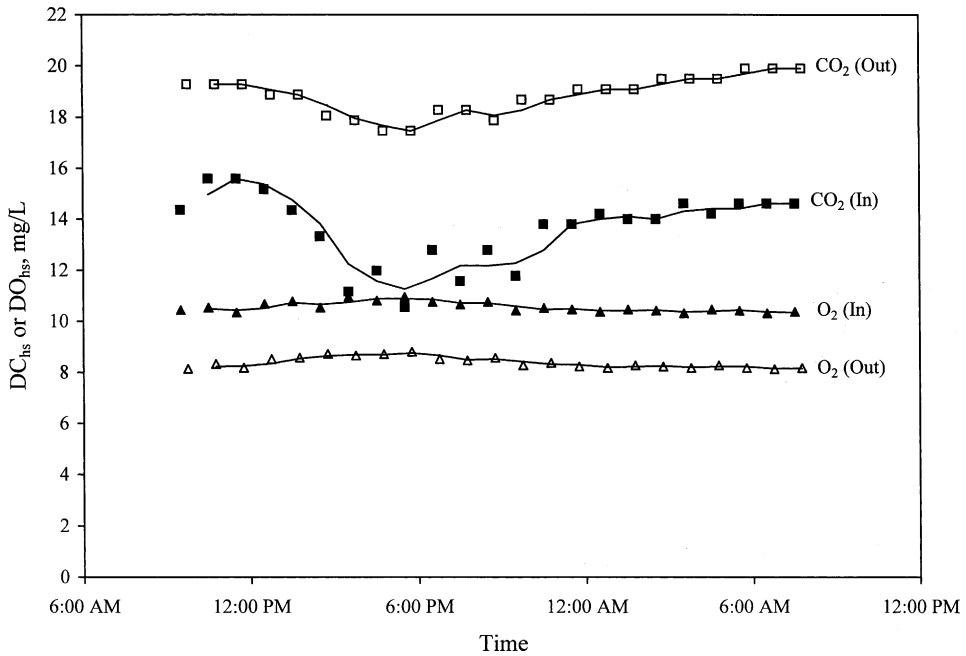


Fig. 8. Changes in dissolved oxygen ( $\text{DO}_{\text{hs}}$ ) and carbon dioxide ( $\text{DC}_{\text{hs}}$ ) across a fluidized bed biological filter during a 24 h period (test series III). Water flow through the filter was about  $4.8 \text{ m}^3/\text{min}$ . This filter supported a design feed rate of 200 kg per day with a make-up flow of 4–6% of the recirculating flow.

6.8 mg/l with a range of 4.0–11.2 mg/l. Mean  $\text{DC}_t$  errors did not vary with monitoring station ( $P > 0.05$ ). Integration of the four replicate instruments with a single meter capable of measuring two gases reduced capital costs per station from US\$ 2920 to 933. This equates to a capital cost of US\$ 467 per gas per station.

## 5. Discussion

Problems linked to wetted probe or titration based dissolved gas analyses can be circumvented through use of instruments designed to establish the equality  $P_i^L = P_i^G$  within a head space chamber (Watten et al., 1997). Here, varying dissolved gas tensions force a change in gas composition as well as total pressure (Eq. (2)). We tested performance of a head space instrument vented to the atmosphere to prevent internal water level fluctuations that result from gas absorption or release. Venting simplified instrument design over that described by Watten et al. (1997), but allows for the condition  $P_i^L = P_i^G$  only when  $\Delta P = 0$  (Eq. (3)). In all other cases ( $\Delta P \neq 0$ ) gas transfer across surfaces provided by water jets (Fig. 1) will cause movement of gas into or out of the head space chamber. The rate of gas transfer is related to the mass transfer coefficient provided by jetting ( $K_{La}$ ), gas type and inlet dissolved gas concentrations relative to saturation concentrations (Lewis and Whitman, 1924; Tsivoglou et al., 1965). Movement of gas prevents the complete equilibration of gas



tension with gas phase partial pressures. Nevertheless, correlations of  $DC_t$  with  $DC_{hs}$  were linear and strong ( $P < 0.001$ ;  $R^2 > 0.98$ ). Test series I data, for example, indicate differences between  $DC_t$  and  $DC_{hs}$  average just 0.9 mg/l, corresponding to a mean relative error of 7%. Precision of  $DC_{hs}$ , as indicated by the coefficient of variation (CV), averaged just 0.97%. Both bias (error) and precision means of the  $DC_{hs}$  method lie within the limit of  $\pm 10\%$  considered acceptable for titration based analyses (APHA, 1998). Bias of the  $DC_{hs}$  estimates was, however, influenced by  $\Delta P$  and alkalinity (Eq. (11)). Thus, application of the method outside of the range of operating conditions tested should be preceded by site-specific comparisons of  $DC_t$  with  $DC_{hs}$ .

Regarding instrument design, head requirements have been minimized (45 cm  $H_2O$ ) to take advantage of the elevation difference that often exists between production system components. This trait eliminates the risk and cost of additional water pumping. Once water flow is initiated, the time required to reach a stable reading is about 9 min. This represents just 10% of the time required to reach equilibrium in an alternate head space instrument that provides for changes in total pressure as well as gas composition (Watten et al., 1997). The improvement in response allows the instrument to follow changes in dissolved gas levels up to a rate of 26 mg/l per hour (Watten, 1992). This ability should provide for the monitoring of DC required when feedback control loops are used to match gas transfer rates with varying gas transfer needs. In this type of application, an ID meter would send a variable voltage signal designed to regulate one or more performance variables, e.g. air flow rate through a  $CO_2$  stripping tower. Commercially available ID meters are capable of monitoring gas streams on a continuous basis while providing needed electrical signal outputs.

When feedback control loops are not applied, a single portable ID like that we tested (Model GD444) could be used to intermittently monitor several stations within a production facility, each outfitted with replicate head space instruments. Here the meter would be moved, as needed, from station to station. The time required to sample head space gas at each station (about 20 s) will, no doubt, represent just a fraction of the time required to estimate DC using the titration method. Alternatively, a single ID can be coupled to several instruments using a timer, valve and tubing system as we demonstrated in test series III (Fig. 3). This latter approach was effective in reducing capital costs per station 67.5% to US\$ 876. Capital costs compare favorably with the current cost of commercially available DC probes (mean, US\$ 3640, range, US\$ 1200–8900,  $N = 4$ ). System performance, during the 21-day trial (test series III), indicated good agreement among  $DC_{hs}$  estimates provided by replicate instruments—the coefficient of variation was just 1.3%. Further, the relative error measured (8.2%) lies again within the range considered acceptable for titration-based analyses, despite elimination of the head space gas return line. In this configuration, we limited gas sampling to 30 s at 30 ml/min. This prevented dilution of gas samples with air drawn through the head space chamber vent tube (Fig. 1). Gas sampling, in our tests, did not promote condensation of water vapor within tubing used to couple system components. This is a potential problem in those applications in which the temperature of the tubing is maintained below that of the gas samples dew-point temperature. Condensation can be avoided here by coupling an in-line water vapor trap to the head space chamber sample port. We used 127 cm long tube to couple our system components. Tubing length can be adjusted to match the site-specific requirements but will influence gas void and pressure

drop. Therefore, changes in tubing length should be accompanied by tests designed to establish required changes in gas sampling rate as well as duration.

In the last phase of test series III, we demonstrated the ability of a single ID meter to measure and log %O<sub>2</sub> and %CO<sub>2</sub>, concurrently. This approach reduced capital costs per gas at each of the four stations 68% to US\$ 467. Increasing the number of stations served can lower costs further, but this will reduce the frequency of gas sampling at each station. The mean error of DO<sub>hs</sub> observed  $-1.1$  mg/l, is higher than the 0.25 mg/l reported for the head space instrument outfitted with a galvanic oxygen sensor mounted directly in the head space chamber (Watten, 1992). The mean error also exceeds the range of error ( $\pm 0.85$  mg/l) reported for a head space instrument that accommodated changes in total pressure as well as gas composition (Watten et al., 1997). Nevertheless, we consider the error observed to be acceptable when DO<sub>hs</sub> is used to control components of intensive production systems. DC<sub>hs</sub> error however, increased to 6.8 mg/l, a level we feel is excessive. The cause of the increase is unknown, but may be related to the use of the HACH method for measuring DC<sub>t</sub> or perhaps the presence of dissolved agents that bias titration analyses (APHA, 1998).

Finally, in test series II, we showed voltage developed by a pH electrode immersed in an isolated sodium carbonate solution that could be used in lieu of an ID to estimate DC<sub>hs</sub>. This method exploits the same chemical equilibria used in commercially available DC probes, but circumvents problems associated with fouling of probe membranes. Further, the relative accuracy and precision established exceeded APHA (1998) criteria for DC<sub>t</sub> analyses, at least over the limited set of operating conditions tested. We feel the method warrants further evaluation prior to application, specifically in the area of SC solution stability. For example, transport of water vapor from the head space chamber into the SC solution, if used over extended periods of time, could alter the [HCO<sub>3</sub><sup>-</sup>]<sup>SC</sup> and hence electrode voltage developed at a given DC concentration (Fig. 5). This potential problem could be avoided by exchanging the SC solution with fresh reagent or perhaps by maintaining gas and liquid phase temperatures that prevent water vapor transport to or from the SC solution reservoir. SC solution temperature should be monitored given temperature effects on both dissociation equilibria and electrode voltage potential. The latter can be avoided with use of compensated probes or predicted based on the Nernst equation (Willard et al., 1981):

$$\text{Electrode potential (mV)} = k - \left( 2.3026 \left( \frac{RT}{F} \right) \right) (\text{pH}) \quad (16)$$

where  $k$  is the line intercept (0.0 mV at pH 7),  $R$  the ideal gas constant,  $T$  the probe temperature and  $F$  the Faraday's constant. This equation predicts that electrode potential will rise from 56.1 mV/pH unit at 10 °C to 60.1 mV/pH unit at 30 °C. The effects of temperature on equilibria pH can be estimated based on application of the Henderson–Hasselbalch equation:

$$\text{Solution pH} = \text{p}K_1 - \log \left\{ \frac{[\text{CO}_2]}{[\text{HCO}_3^-]} \right\} \quad (17)$$

where  $\text{p}K_1$  is the negative logarithm of the equilibrium constant for the protolysis of H<sub>2</sub>CO<sub>3</sub>, [CO<sub>2</sub>] is DC in moles/l and [HCO<sub>3</sub><sup>-</sup>] is bicarbonate in moles/l. Values of  $\text{p}K_1$  decrease as temperature increases (Lowenthal and Marasi, 1976) causing a similar shift in pH (Eq. (17)). For example, with [CO<sub>2</sub>] and [HCO<sub>3</sub><sup>-</sup>] fixed at 0.57 and 2.0 mmol/l, respectively, an increase in temperature from 10 to 30 °C reduces SC solution pH from 7.02 to 6.89. This

corresponds to a change in electrode potential of about 8 mV assuming that the electrode has been compensated for the temperature rise. Temperature corrections can easily be incorporated into software supporting the monitoring and logging of electrode output (mV).

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## References

- APHA (American Public Health Association, American Water Works Association, and Water Pollution Control Federation). 1998. Standard methods for the examination of water and wastewater, 19th edn. American Public Health Association, New York, USA.
- Basu, S.P., 1959. Active respiration of fish in relation to ambient concentrations of oxygen and carbon dioxide. *J. Fish. Bd. Can.* 16, 175–212.
- Bouck, G.R., 1982. Gasometer: An inexpensive device for continuous monitoring of dissolved gases and supersaturation. *Trans. Amer. Fish. Soc.* 111, 505–516.
- Colt, J., Orwicz, K., 1991. Modeling production capacity of aquatic culture systems under freshwater conditions. *Aquacult. Eng.* 10, 1–29.
- Colt, J., 1984. Computation of dissolved gas concentrations in water as functions of temperature, salinity and pressure. *Amer. Fish. Soc.*, Bethesda, Maryland, special publication, no14.
- Haug, R.T., McCarty, P.L., 1972. Nitrification with submerged filters. *J. Wat. Poll. Contr. Fed.* 44 (11), 2086–2102.
- Lewis, W.K., Whitman, W.C., 1924. Principles of gas absorption. *J. Ind. Eng. Chem.* 16, 1215–1220.
- Lowenthal, R.E., Marasi, G.V., 1976. Carbonate chemistry of aquatic systems, theory and application. Ann Arbor Science Publishers, Ann Arbor, MI, USA.
- Smart, G.R., Knox, D., Harrison, J.G., Ralph, J.A., Richards, R.H., Cavey, C.B., 1979. Nephrocalcinosis in rainbow trout *Salmo gairdneri* Richardson: The effect of exposure to elevated CO<sub>2</sub> concentrations. *J. Fish. Diseases* 2, 279–289.
- Speirs, G.D., Chapman, E., Matthews, J., 1986. The calibration and evaluation of dissolved oxygen sensors in a pilot scale activated sludge plant. In Boyl, W.C. (Ed.), *Aeration Systems*. Noyes Publications, Park Ridge, NJ, USA, pp.243–260.
- Swinerton, J.W., Linnenbom, V.J., Cheek, C.H., 1962. Determination of dissolved gases in aqueous solutions by gas chromatography. *Anal. Chem.* 34 (4), 483–485.
- Tsivoglou, E.C., O'Connell, R.L., Walter, C.M., Godsil, P.J., Logsdon, G.S., 1965. Tracer measurements of atmospheric reaeration-1. Laboratory studies. *J. Wat. Poll. Contr. Fed.* 37, 1343–1362.
- Watten, B.J. 1992. Feasibility of monitoring dissolved oxygen based on gas-phase partial pressures. Published abstract. *Aquaculture* 92. May 21–25, Orlando, FL USA.
- Watten, B.J., Ridge, W.J., Mudrak, V.A., 1994. Effect of subatmospheric pressure on the performance of an automated packed-column nitrogen desorption system. *Aquacult. Eng.* 13, 41–58.
- Watten, B.J., Smith, D.R., Ridge, W.J., 1997. Continuous monitoring of dissolved oxygen and total dissolved gas pressure based on head space partial pressures. *J. World Aqua. Soc.* 28 (4), 316–333.
- Willard, H.H., Merritt, L.L., Dean, J.A., Settle, F.A., 1981. Instrumental methods of analysis. Wadsworth Publishing, Belmont, CA, USA.
- Williams, D.D., Miller, R.R., 1962. An instrument for on-stream stripping and gas chromatographic determination of dissolved gases in liquids. *Anal. Chem.* 34 (6), 657–659.